

THE STABILITY OF ESTER TYPE PLASTICIZERS.

II. THE INFLUENCE OF INORGANIC FILLERS AND PIGMENTS
ON THE VOLATILITY OF PHTHALIC ACID PLASTICIZERS.

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THE STABILITY OF ESTER TYPE PLASTICIZERS II¹ THE INFLUENCE
OF INORGANIC FILLERS AND PIGMENTS ON THE VOLATILITY OF
PHTHALIC ACID PLASTICIZERS

Z. Wolkober

ABSTRACT: The volatility of plasticizers is the result of physical transport processes and decomposition processes induced by oxidation. The volatility loss in PVC-plasticizer mixtures is significantly higher than that of the plasticizers alone. Pigments and fillers increase considerably the volatility of plasticizers. The bisphenol A as antioxidant decreases the volatility loss of the PVC-plasticizer system. The irradiation with a xenon lamp causes also a measurable volatility loss even at room-temperature, and this loss is especially high in the presence of anatase titanium dioxide.

The functional properties of PVC plasticizers can be judged from several points of view:

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- a) The effect of the plasticizer on the processing of the PVC plasticizer system;
- b) The effect of the plasticizer on the physical properties of the finished product (mechanical strength, electrical properties, etc.);
- c) The effect of the plasticizer upon the stability of finished products made with the system (heat resistance, weather resistance, etc.);
- d) The volatility and chemical stability of the plasticizer.

Professional literature deals extensively with the properties mentioned in a) and b). Scarcely any data can be found in the literature concerning the stability of PVC based plasticizer systems or the stability of the plasticizers themselves.

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The volatility of plasticizers in close relationship to their tension, while their chemical stability is primarily characterized by their behavior in respect to oxidative processes.

Because of the physical instability the plasticizers evaporate as a result of transport processes in a chemically unvaried form or evaporate from the PVC based systems.

As a consequence of the chemical instability a change occurs in the valence bond of the plasticizers. This can occur in two directions: in the presence of oxygen it is thermo oxidative or photo oxidative, while in the absence of oxygen it is thermodegradative.

The plasticizer can also effect the PVC stability. The decomposition products resulting from the plasticizer instability had a detrimental effect upon the stability of the PVC based systems.

As a result of the oxydation and incidental thermal degradation the plasticizer components of greater tension break down and this leads to a tangible increase in plasticizer volatility. Antioxidants reduce the volatility induced by oxidation, but the antioxidants do not have any effect upon thermodegradative or physical volatility.

The purpose of our experimental work described below was to examine the physical and chemical volatility of plasticizers of a phthalate type in the presence of antioxidants or inorganic pigments.

Review of the Literature

The stability of the plasticizers used in PVC is just as important as the stability of the PVC itself. However, even the newest data in the literature do not deal as seriously with plasticizer stability as would be justified [1-9].

Plasticizers can suffer physical and chemical change during treatment and use. Of the changes of a physical nature the most important is evaporation. Generally the technical literature associates evaporation loss with plaster tension, but does not consider the fact that in the simplest volatility examinations the physical and chemical processes coalesce [10-13].

Two factors effect plasticizer volatility:

- a) The physical stability of the plasticizer;
- b) The chemical stability of the plasticizer.

Under identical circumstances the plasticizer tension determines the physical stability. Chemical resistance to oxidative and degradative processes depend upon plasticizer structure and is essentially linked to the magnitude and structure of the alchohol part of the plasticizer.

Thinius deals thoroughly with plasticizer volatility [1]. He has published many data concerning the tension of various kinds of plasticizers. Although the tension index has been determined thermodynamically, the volatility indices measured by different authors at the same temperature do not agree well. The cause of this fact is that the volatility loss does not depend only on the vapor tension formed above the plasticizer; as a result of the chemical processes subsequent changes in weight depending on the test conditions are also contributory, since the volatility loss is the result of both. Depending upon weather the transport processes or the chemical processes dominate the plasticizer test, a difference in magnitude can occur among various volatility indices.

Thus we must consider as a fundamental point the fact that while it is possible to increase physical volatility at will by using transport processes- greater specific surface, greater gas circulation-, processes, for the most part oxidative, operating under identical conditions do not function at all, or very slightly, with an increase in specific surface.

We can find numerous items in the literature about the volatility loss of plasticizers without additives. Some of the methods used measure the volatility loss with an activated carbon, while some authors determine the loss with a Brabender type "rapid water determination device" [16, 17, 18].

Examination time is short with the activated carbon process, but the test results are unusually widespread, depending on the quality of the activated carbon used. In the Brabender type determination the oxidative and transport processes occur parallel to one another if the test is not made in an inert atmosphere.

At all events it can be stated that in examining plasticizer volatility there is no satisfactory method for separating the physical and chemical processes from one another.

In examinations on plasticizer stability Krekeler has shown that plasticizer volatility in the presence of several thousandths of an antioxidant (diphenyl prophane) is reduced by orders of magnitude. This suprising experimental fact can only be attributed to a suspension of chemical processes following the effect of thermal stress [19].

De Coste and Wallder [20, 21, 22] examined the weight variation in foils containing various plasticizers in pigments aged under natural and artificial conditions. They showed that the volatility loss of foils of identical composition but containing 2% titanium dioxide of a carbon black or rubile type is only a fraction that of nonpigmented foils produced under identical conditions. In this case the pigments protected the plasticizer from photo oxidation. Their observation that diphenylolpropane (dian) did not reduce the volatility loss of plasticizers is significant. This can be attributed either to the fact that the dian was removed from the foil under the test conditions or that the simple antioxidant is ineffective against photo oxidative processes.

Zilbermann and Sztuzsakov investigated the thermal decomposition of phthalic acid esters [23]. In the case of dioctyl phthalate they demonstrated the formation of the decomposition products below by means of chromatographic analysis; 3-methylene heptane, 3-methyl-heptane-2, 3-methyl-heptane-3 and 2 methyl hexyl alcohol. When dioctyl phthalate is decomposed thermally in the presence of acid of PVC, 2-ethyl hexonal is not formed, but rather unsaturated hydrocarbons and phthalic acid.

Murfit and his colleagues examined alkyl ester oxidation and analyzed the decomposition products and came to the conclusion that the oxigen consumed is incorporated chiefly in the form of peroxides [24].

In his monograph Chevassus has already dealt in detail with the reciprocal influences of other plasticizers and PVC ingredients and with plasticizer

stability [3]. The information mentioned here indicates that plasticizer volatility is essentially the result of chemical reactions with phthalates of greater molecular weight.

Roessig reports on the volatility of various plasticizers at different temperatures [12]. A surprising experimental result is the fact that plasticizer volatility in PVC foils is essentially greater than it is by itself. Even though he used different methods to determine the volatility loss with PVC and plasticizers, his tests still show that in the presence of PVC the plasticizer decomposes to a much greater extent, from both thermal and photo oxidative causes, than by itself.

A great deal of data in the literature deals with the stability of plasticized PVC systems as a function of the pigment used, but these investigations refer to determinations of the properties of the products, without considering the fact that the deterioration of the products is the result of PVC decomposition or of the plasticizer instability [25].

Without further detail we provide in our references some of the more important and more recent data in the literature dealing with plasticizer properties and stability [26-43].

Experimental Method

During our work on the stability of PVC based systems, we investigated the reciprocal effects of the plasticizer-PVC-filler system with special attention to the volatility losses of plasticizers. In the technical literature we did not find any information pertaining to this relatively simple measurement, although during our experiments in other directions it became absolutely clear that the stability of plasticizers against oxidation depends to a very large extent on the common fillers used. On the other hand - and on the bases of data in the literature - it may be presumed that there is a connection between plasticizer stability against oxidation and volatility, influenced to a large degree by the pigments used. Accordingly we carried out tests of the following types:

1. We tested the volatility loss of several plasticizers without additives or containing dian at 100° C,

2. In the case of PVC-plasticizer in a 1:1 mixture in the presence of various kinds of fillers we determined the volatility at 100° C,

3. In the case of a mixture of PVC and plasticizer in a 1:1 ratio in the presence of various kinds of filler we determined the volatility loss at 30° C with a brightness of 100,000 lux.

We carried out our observations for number 1 with a very simple method. We prepared a vessel with a surface $6 \times 8 = 48 \text{ cm}^2$ 0.1 mm thick of aluminum foil which was first cleaned and we rubbed uniformly into it 0.5000 grams of plasticizer, and then weighed it with analytical exactitude; finally we placed it in a water bath with sides 1 cm high and with a flat surface under 100° C reflux. We must mention that the sides of the aluminum vessel must be constructed in such a way that they do not form sharp angles because in this case, as a consequence of capillarity, the plasticizer will draw up the walls. This method is suitable for determining the volatility loss of plasticizers and of plasticizers with various kinds of antioxidants and for comparing them. This experimental method gives the complete volatility loss, but by examining the antioxidant containing plasticizers we can find the relationship between antioxidant stability and volatility. The volatility loss of the plasticizers can be determined within experimental limits of a maximum of 5%.

Observation time can be reduced by about 30% if we place the plasticizer in the aluminum vessel on fiberglass and determine the volatility loss in this way. In consideration of the fact that the fiberglass means another uncertain factor in our tests, but without considerably reducing measurement time, we carried out all later measurements without fiberglass.

The reciprocal effect of plasticizers and fillers cannot be examined together in this way, because during the test the fillers precipitate and thus we cannot get very reproducible results.

We carry out our tests for number 2 on the plasticizer-PVC systems in the following way: we prepared a paste from the 1:1 mixture of plasticizer and PVC, measured out 1 gram of it on the aluminium vessel, then jelled it at 160° C, afterwards measuring it again, placing it in a 100° C water bath and occasionally determining the loss of weight which had occurred. In this case again, we found a volatility loss of 0.5 grams of plasticizer.

Measuring the plasticizer-PVC-filler systems was the same as above. In this case also we collated the volatility loss with the plasticizer in the system.

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Our tests on the photo chemical volatility of the PVC-filler-pigment system according to 3 were carried out with Xeno test WL equipment. In this case we prepared a plaster from the PVC-plasticizer mixture in the 1:1 ratio and jelled it on aluminium foil. We determined the weight with analytical exactitude, then placed it on the Xeno test operating at 32° C and from time to time determined the loss of weight which had occurred.

We use the following material in our tests:

Chemical name	Abbreviation	Proprietary name	Manufacturer
Diisooctyl phthaalate (free of antioxidant)	DIOP	Kábelipari extra	Egyesült Vegyi- művek
Dibutyl phthalate	DBP	Palatinol C	BASF
Diisobutyl phthalate	DIBP	Palatinol IC	BASF
Polyvinyl chloride	PVC	Halvic 336	Austrian
Dihydroxyl diphenylol propane	DIAN	Bisphenol A	Hungarian

Fillers:

Asbestos SU K-7
Crushed Kaolin
Prepared chalk
Barite
Precipitated chalk

Pigments:

Anatase type TiO_2
Rutile type TiO_2
Carbon black
Red iron oxide I
Red iron oxide II
Yellow iron oxide I
Yellow iron oxide II
Black iron oxide I
Black iron oxide II
Channel black

We designate the fillers and the pigments only by composition, not by their commercial names. Actually commercial products are not included since it is not known in what way they might affect the volatility of the fillers or pigments. It was not the purpose of our investigations to determine weather additives from different batches but with the same commercial names always effect volatility stability in the same way. This will be another problem, the aim of which will be to determine the relationship between the physical and chemical characteristics of pigments and fillers and results on stability. Thus not reviewed here, particularly relative to various varieties of CaCO_3 , indicate, e.g., that with natural and artificial kinds of chalk it is not the chemical composition, but the physical form and the possible presence of impurities and additives which are the decisive factors.

Evaluation of the Results

Percentage evaluations of volatility loss depend essentially upon the amount of test material and upon its surface. In order to justify this fact we weighed the plasticizer of 0.5-10 grams in the aluminium vessel of standard measurements (48 cm^2) chosen by us and a mixture of plasticizer-PVC in a 1:1 ratio and examined the volatility loss. The test results can be seen in table one.

Volatility Loss of DIBP and DIBP-PVC of Various Weights at 100° C

Weight	0,5 g		1,0 g		5,0 g		10,0 g	
time, h	Volatility loss percentage							
	DIBP	DIBP-PVC	DIBP	DIBP-PVC	DIBP	DIBP-PVC	DIBP	DIBP-PVC
2	4,34	14,4	2,28	7,84	0,47	1,58	0,26	0,68
4	7,12	23,6	4,73	15,4	1,05	2,78	0,44	1,20
6	10,5	33,8	8,30	22,4	1,63	3,98	0,68	1,72
10	18,0	55,6	14,6	39,0	2,80	6,15	1,12	2,65
20	47,3	79,2	32,8	63,6	5,05	11,6	2,21	4,80
24	60,0	80,0	38,7	70,0	6,06	13,7	2,64	5,48
48	95,2	86,6	57,3	83,0	13,0	20,3	5,99	10,3

This series of tests shows without exception that, in examining the volatility loss of plasticizer, standard conditions must be maintained as strictly as possible, since otherwise test results can occur which differ enormously from one another. It must be stated as an exceptionally important and essential experimental fact that the volatility of plasticizer and PVC is significantly greater than that of the plasticizer alone.

This phenomena can be explained by the fact that in the plasticizer-PVC system, in comparison to the pure plasticizer, there appear new intramolecular reciprocal effects. In the case of pure plasticizer only a plasticizer-plasticizer bond is possible but in the plasticizer-PVC system there are already 3 kinds of bonds; there is interaction:

Between plasticizer-plasticizer moecules,

Between plasticizer-PVC moecules,

Between PVC-PVC molecules.

A strong intermolecular bond occurs between the plasticizer molecules. This reduces the tension and thus reduces volatility.

In the plasticizer-PVC systems a weaker bond occurs between the plasticizer and PVC molecules which can probably be explained by the fact that the plasticizer volatility in the plasticizer PVC system is essentially greater than in the pure state.

Among the antioxidants we examined the effect of dian in reducing volatility and have presented in Figure 1 the DIOP volatility loss in the presence of various amounts of antioxidants.

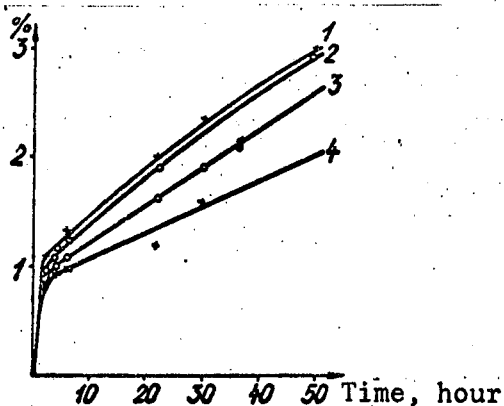


Figure 1. DIOP volatility loss at 100°C in the presence of various amounts of antioxidants.

1 DIOP by itself; 2 DIOP + 0.01% dian;
3 DIOP + 0.1% dian; 4 DIOP + 0.5% dian.

It can be stated on the basis of these tests that the DIOP in the amount of about 1% contains other materials of greater volatility (alcohol, water, etc.) the volatility of which the antioxidant naturally does not affect. Dian significantly reduces DIOP volatility in a proportion equal to the concentration used. This series of tests, along with many others, unambiguously verified the fact that the volatility and oxidation of plasticizers are functions of one another.

Figure 2 shows the volatility loss of DIBP and DBP, as well as of the two mixtures formed of plasticizer with PVC, again at 100° C.

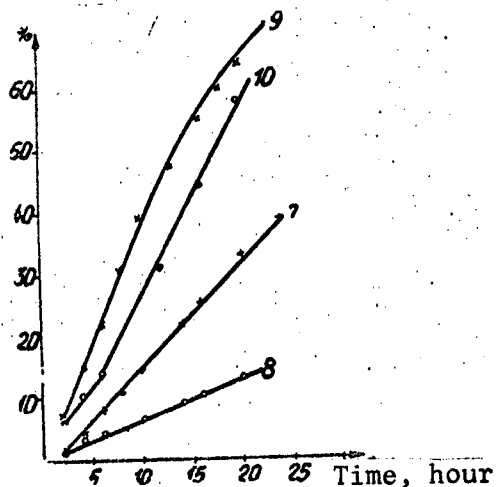


Figure 2. The volatility loss of DBP (Palatonal C) and of DIBP (Palatonal IC) by themselves and in the presence of PVC.
 7 DIBP by itself; 8 DBP by itself; 9 DIBP + PVC in a 1:1 mixture; 10 DBP + PVC in a 1:1 mixture.

On the one hand the data from Figure 2 show that there is a significant difference between the volatility of DBP and DIBP, but on the other hand contained newer data pertaining to the fact that the plasticizer volatility in PVC is essentially greater than by itself.

In Figure 3 we have shown the data relating to the volatility of the DIBP-PVC-dian system.

Again the experimental data point unambiguously to the fact that in plasticizers with or without PVC the antioxidant reduces the volatility loss.

During our tests on the volatility of the PVC-DOP-dian system we obtained results of a similar nature. Although the DOP volatility is a fraction that of the DBP volatility, the volatility loss still increases in the presence of PVC and diminishes in the presence of dian.

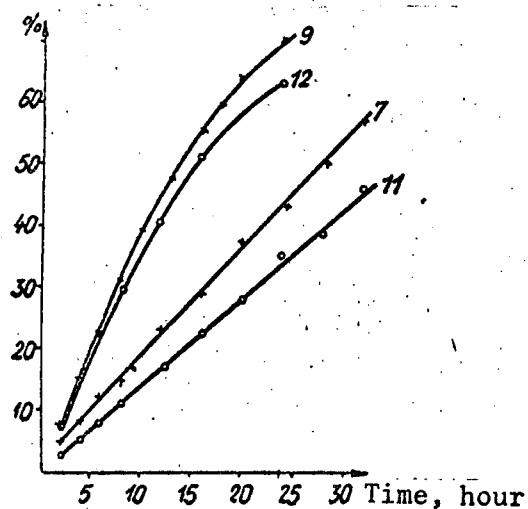


Figure 3. Volatility loss of DIBP-PVC-dian system at 100° C.
7 DIBP by itself; 9 DIBP + PVC in a 1:1 mixture; 11 DIBP + 0.1% dian; 12 DIBP + PVC + 0.1% dian.

Considering the fact that from the viewpoint of the synthetic industry DIOP is much more important than DBP, we used the Egyesult Vegyimuvek cable industry DIOP in our tests of the PVC-plasticizer-filler system; the DIOP-PVC ratio was 1:1 and the test temperature was 100° C. Some data from our tests in the direction are shown in Figure 4.

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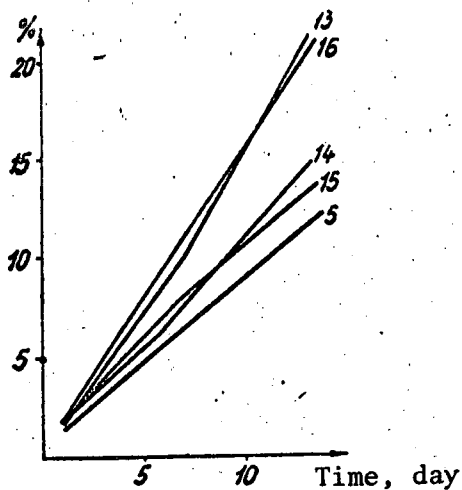


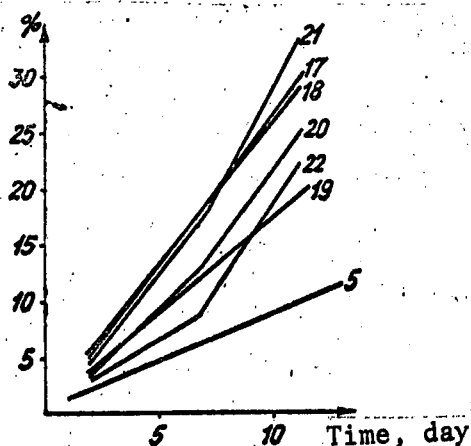
Figure 4. Volatility loss of DIOP-PVC system in the presence of different pigments at 100° C.
5 DIOP-PVC; 13 DIOP-PVC + 10% anatase; 14 DIOP-PVC + 10%; 15 DIOP-PVC + 2.5% carbon black; 16 DIOP-PVC + 10% asbestos.

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The data in the figure show that the pigments tangibly affect the volatility losses of the plasticizers. We must emphasize the effect of the anatase of the TiO_2 type and of the asbestos, in the presence of which the volatility loss is about doubled. The most favorable result is provided by the carbon black or the rutile of the TiO_2 type, but even in the presence of these materials the volatility loss is greater than in the mixtures without pigments.

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Various kinds of iron oxide pigments are widely used in the synthetic material industry. In Figure 5 we have shown the volatility loss values measured in the presence of some kinds of iron oxide.



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Figure 5. Volatility loss in the DIOP-PVC system in the presence of various iron oxide pigments at 100°C .

5 DIOP-PVC; 17 DIOP-PVC + 10% red iron oxide I.; 18 DIOP-PVC + 10% red iron oxide II.; 19 DIOP-PVC + 10% yellow iron oxide I.; 20 DIOP-PVC + 10% yellow iron oxide II.; 21 DIOP-PVC + 10% black iron oxide I.; 22 DIOP-PVC + 10% Hungarian iron oxide II.

It can be stated that the different kinds of iron oxide hastened the plasticizer evaporation to a suprisingly large degree: compared with the pigment-free mixtures, the plasticizer loss increases 6 or 7 times in the worst situation. We present some test data relating to the effect of several fillers in Figure 6.

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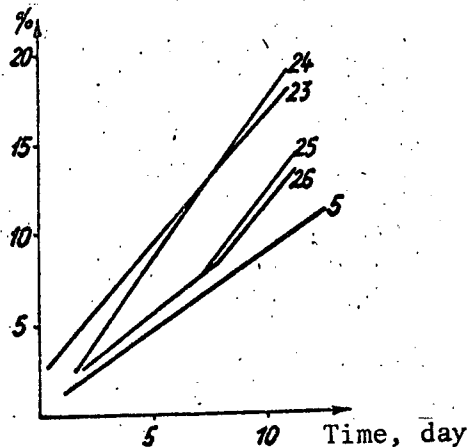


Figure 6. Filler effect upon the volatility loss of the PVC-DIOP system at 100° C.
 5 PVC-DIOP; 23 PVC-DIOP + 10% crushed kaolin; 24 PVC-DIOP + 10% prepared chalk Omya BSH; 25 PVC-DIOP + 10% Barite; 26 PVC-DIOP + 10% precipitated chalk.

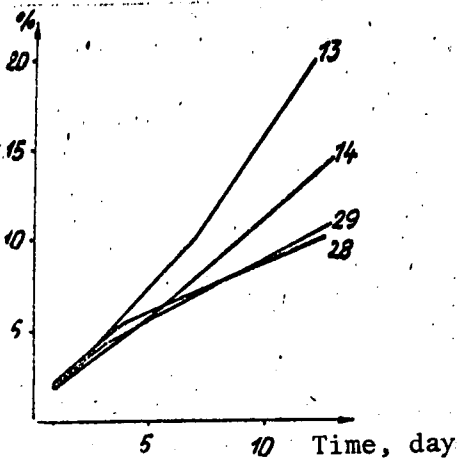


Figure 7. The effect of dian on the volatility loss of the PVC-DIOP system at 100° C.
 13 PVC-DIOP + 10% anatase; 14 PVC-DIOP + 10% rutile; 28 PVC-DIOP + 10% anatase + 0.1% dian; 29 PVC-DIOP + 10% rutile + 0.1% dian.

According to the data in the figure the fillers without exception likewise increase volatility loss, although generally to a lesser extent on the different kinds iron oxide.

The dian also diminishes the volatility of the PVC-DIOP-filler system. In Figure 7 we have included some pertinent test values.

In this case the experiments also show that the dians likewise sharply reduces the volatility loss of plasticizers in the case of pigments with a titanium oxide base.

We also carried out some instructive examinations of the photo oxidative volatility of the plasticizers. Taking into consideration the fact that the thermo oxidative and photo oxidative processes differ considerably in nature and degree, we used the Xenotest equipment to determine the volatility loss of the PVC-DIOP system in the presence of several pigments at 32° C with 100,000 lumens illumination. Figure 8 summarizes the pertinent measurements .

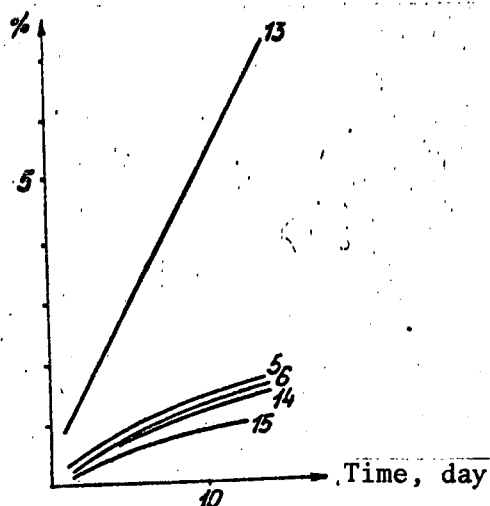


Figure 8. The Volatility loss of the PVC-DIOP pigment system with Xenotest equipment at 32° C. 5 PVC-DIOP; 6 PVC-DIOP + 0.1% dian; 13 PVC-DIOP + 10% anatase; 14 PVC-DIOP + 10% rutile; 15 PVC-DIOP + 2.5% channel black.

This test shows that rather large volatility losses can occur at even low temperatures with allumination approaching daylight, and this is increased several times by titanium dioxide of the anatase type and considerably reduced by TiO_2 of the rutile type or carbon black. Attention is also attracted by the fact that the dian does not have any essential effect upon the volatility loss of the systems, a test result which agreed with De Costa's data.

SUMMARY

One form of ageing of soft PVC systems containing fillers is plasticizer evaporation. The evaporation is composed of chemical and physical factors and depends to a great degree on the amount of filler or pigment present, and on the resistance the plasticizer has shown to oxidative and degradative processes.

The stability of the plasticizer-filler system against oxidation can be considered a special kind of polyphase catalysis. This property is particularly important in the PVC-plasticizer-filler system, but some rather new interactions occur here, the nature of which we still understand quite poorly. It is an indisputable fact that antioxidants lessen volatility loss, and this unambiguously demonstrates the chemical nature of volatility.

Physical and chemical volatility are related. The volatility of very volatile plasticizers operating with slight physical stability is barely or not at all effected by antioxidants. The time sufficient for plasticizers of great physical stability is convenient for the action of harmful chemical processes leading in this case to volatility of an oxidative origin. The volatility losses occurring in this way can be impeded by antioxidants.

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The situation with fillers and pigments is similar. In plasticizers of slight physical volatility or great oxidational stability the fillers do not have enough time to allow harmful or advantageous effects. For this reason the choice of fillers and pigments is much more important for systems with a great physical stability.

The volatility caused by light is also the result of oxidative processes, but its kinetics differ fundamentally from thermal oxidation. While, e.g., thermal volatility is harmed to a lesser degree by rutile type TiO_2 and to a greater degree by anatase type TiO_2 the anatase increases photochemical volatility about 5 times, while rutile reduces it to a slight degree. Dian, which has worked well against thermal oxidation, is almost ineffective in the case of photo oxidation.

Without exception the tests referring to the oxidative stability or volatility stability of plasticizers show that the individual components of the soft PVC systems affect the stability of each other in a complicated way, so that it is absolutely necessary to know the properties and interactions of the individual components in order to distinguish the factors affecting stability.

In addition the chemical and physical stability of the plasticizers, the effect produced on the systems by other additives (filler, pigment, etc.) belong to the total picture of the stability of PVC based systems containing plasticizers.

According to the tested data referring to the stability of soft PVC based systems, the stability tests must be extended to the physical and chemical stability of the plasticizers and to the quality of the fillers and pigments.

At this point I wish to thank the Muanyagipari Kutato Intezet [Research Institute of the Synthetic Industry] which made it possible for the tests reported here to be carried out, and likewise to all working comrades who assisted me in large measure in carrying out this experimental work.

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